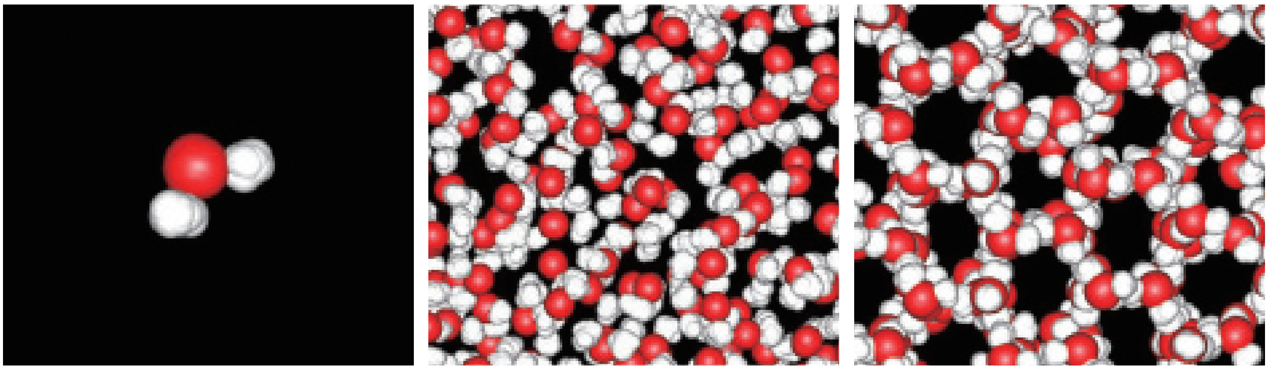
10-5 Why Water Can't Be Heated or Cooled Easily?

－A Molecular Theory for the Specific Heat of Water－



(a) Vapor (b) Liquid water (c) Ice (I_h phase)

Fig.10-7 Red and white spheres indicate oxygen and hydrogen atoms, respectively
By molecular dynamics simulation, the motion of molecules is analyzed in a computer.

Water is a ubiquitous chemical substance used in a vast range of research fields, from atomic energy to biology, but it possesses special characteristics that other substances do not have. For instance, as one of the 'anomalous' properties of water, it is known that the specific heat of water changes drastically according to the temperature and phase. At the melting point, the specific heat of liquid water becomes twice as large as that of the ice. Meanwhile, at the boiling point, the specific heat of vapor decreases to 1/3 that of liquid water. Liquid water has unusually large specific heat compared to other substances(about 4.19 J/gK, 1 cal/g℃) and it does not vary much by temperature. On the other hand, the specific heat of ice and vapor changes dramatically with temperature; It tends to increase with temperature both in the case of ice and vapor. It is known that heavy water has a larger specific heat than light water by about 10 % for a unit mol. How can these facts be understood from the view point of molecular theory?

As shown in Fig.10-7, water molecules, composed of hydrogen and oxygen atoms, form weak bonds (hydrogen bond) between each other. In liquid water, the creation and annihilation of these hydrogen bonds are perpetually repeated, causing complex motions. In addition, the light hydrogen atoms behave quantum mechanically. Although it can be expected that these factors affect the specific heat, this has never been actually confirmed by a theoretical simulation. Therefore, in this study, a molecular dynamics simulation has been performed for a quantitative analysis on the specific heat of the three states of water.

From this study, it has been found that there are two important factors in the specific heat of water. One is the 'strength' of hydrogen bonds. In the condensed phases, ice and liquid water, the molecular vibrations of individual molecules are induced and the hydrogen bonds are weakened as temperature is increased. The specific heat is determined by how much of the energy given by an external heat source the molecules can absorb. In the case of ice, the hydrogen bond is so firm that the whole molecule pair will be vibrated without absorbing much heat. However, liquid water can absorb more heat through the transforming or breaking of hydrogen bonds. In other words, it is because the hydrogen bonds play a role of large 'heat bath' that makes the specific heat of liquid water large and constant. In the vapor phase, since water exists as isolated molecules without hydrogen bonds, the specific heat is small since the 'heat bath' is small.

Another factor is that the mechanics of hydrogen bonds changes from classical mechanics to quantum mechanics as temperature is decreased. The bond with 'quantum nature' has a tendency to absorb less heat, because the vibrational energy levels become discrete and thus the molecular excitation is rather limited. This is why the specific heat tends to decrease with temperature.

The specific heat of water is realized by two factors: the 'strength' and 'quantum nature' of hydrogen bonds. Incidentally, the difference of specific heat between light and heavy water can also be explained by these two factors.

Reference

Shiga, M. et al., Calculation of Heat Capacity of Light and Heavy Water by Path Integral Molecular Dynamics, Journal of Chemical Physics, vol.123, no.13, 2005, p.134502-1-134502-8.